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*Polymer Degradation III. Carbon-14 as a
Tracer for Studies of the Thermal
Degradation of Polyurethans*

*R. Simha
J. D. Ingham
N. S. Rapp
J. Hardy*

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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The use of tracers for the study of polymer degradation reactions constitutes a powerful approach, particularly for polymers that possess a variety of bond types that may result in complex mechanisms of degradation. Previous work has indicated that polyoxypropylene glycol-toluene diisocyanate (PPG-TDI) polymer degrades predominately by a random scission process in the absence of oxygen at $\sim 200^{\circ}\text{C}$. to regenerate hydroxyl and isocyanate. However, because of several bond types and possible side reactions, random kinetics are not obtained (1,2).

Therefore, to examine the utility of tracer applications for degradative studies and to determine further details of the degradative process for PPG-TDI, experiments with polymers prepared from carbon-14-labeled diisocyanates have been initiated. This paper presents some preliminary results obtained for PPG-TDI containing carbon-14.

TDI was prepared from 2,4-toluene diamine and phosgene containing carbon-14 (3). Six- to eight-gram polymer samples were prepared and intrinsic viscosities and molecular weights were estimated by methods given previously (1,2). The PPG used had a number-average molecular weight of ~ 2000 . During degradation, dry nitrogen was passed through the polymer at a flow rate of 100 ml./min. Carbon-14 in the residues was counted with a Packard Tri-Carb liquid scintillation counter in di-

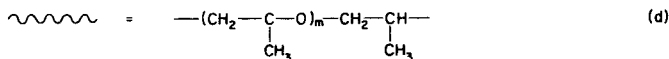
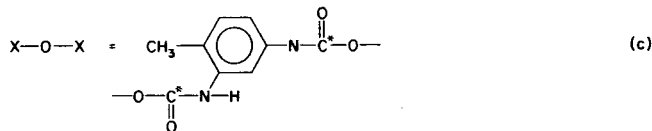
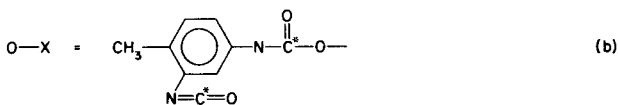


Figure 1

*This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under the Advanced Research Projects Agency, Letter Order No. 107-62, for the National Aeronautics and Space Administration.

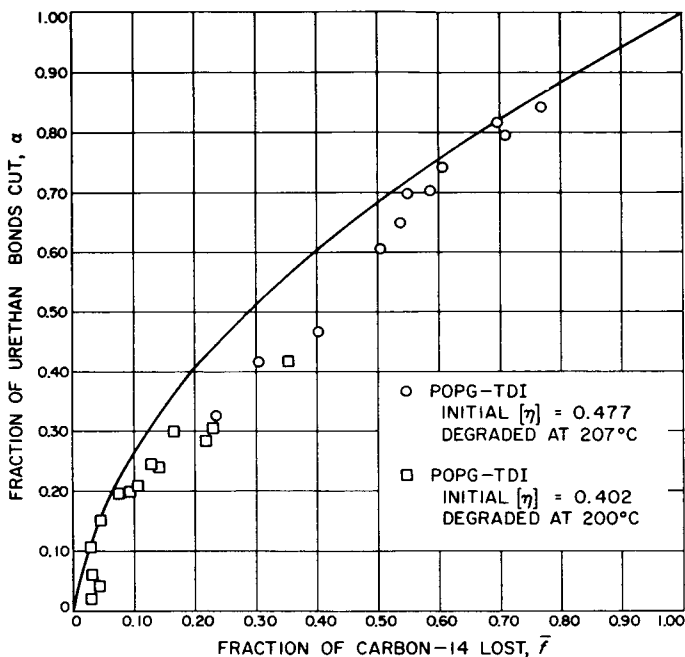


Fig. 2. Degradation of POPG-TDI: urethan scission versus C^{14} evolved.

lute toluene solution, the primary and secondary scintillators being PPO (2,5-diphenyloxazole, 5g./l.) and dimethyl POPOP [1,4-bis-2(4-methyl-5-phenyloxazolyl)-benzene, 0.3 g./l.], respectively.

An idealized PPG-TDI molecule is represented schematically (a) in Figure 1, with (b), (c), and (d) showing the structural units in the chain. The labeled carbons are those that are linked to a nitrogen atom. If only urethan bonds break, which is a reasonable assumption at $\sim 200^\circ\text{C}$. (1,2), the relationship between the carbon-14 lost and the number of scissions can be derived; however, its form depends on the relative rates of scission of nonequivalent urethan bonds. If it is assumed that the rate of scission is the same for all types of urethan present in PPG-TDI, and that the TDI formed is volatilized, then an expression for \bar{f} , the fraction of carbon-14 or TDI volatilized, in terms of α , the fraction of urethan bonds cut, can be obtained as follows. The total number of urethan bonds N_b (the X's in (a) of Fig. 1) for undegraded polymer is given by:

$$N_b = 2 (M_{n(0)} - M_t) / M_u \quad (1)$$

in which $M_{n(0)}$ is the initial number-average molecular weight, M_t is the

TABLE I
 Degradation of Polyoxypropylene Glycol-Toluene Diisocyanate Polymer:
 Change in Intrinsic Viscosity and Carbon-14 Activity at 207°C.

Time, hr.	Intrinsic Viscosity [η], dl./g.	C ¹⁴ Activity, counts/min./g.	Wt. av. mol. wt., ^a M_w	No. av. mol. wt., ^b M_n	No. of cuts, ^c S	Fraction of bonds cut, α ^d	Fraction of C ¹⁴ activity lost, \bar{f}
0	0.477	279,000	61,000	31,587	0	0	0
24	0.147	226,000	9,700	5,973	4.32	0.319	0.235
48	0.124	194,000	7,500	4,837	5.53	0.409	0.305
72	0.113	167,000	6,500	4,337	6.28	0.464	0.402
144	0.0092	138,000	4,700	3,437	8.19	0.605	0.506
168	0.087	129,000	4,300	3,237	8.76	0.647	0.538
192	0.082	126,000	3,500	3,037	9.40	0.695	0.549
218	0.081	115,000	3,550	3,012	9.49	0.701	0.588
239	0.077	109,000	3,550	2,862	10.04	0.742	0.610
357	0.072	80,000	3,200	2,687	10.76	0.795	0.714
405	0.070	84,000	3,070	2,622	11.05	0.817	0.699
500	0.068	64,000	2,920	2,547	11.40	0.843	0.771

^a Calculated from $[\eta] = 0.413 \times 10^{-4} M_w^{0.64} (1,2)$.

^b From $M_n = (M_w + M_u)/2$, where $M_u = 2174$. (Although there are 2 urethan bonds per 2174 in molecular weight, 2174 may be taken for M_u because after scission of a given urethan bond a cut at the urethan that was adjacent to it does not effectively decrease $[\eta]$.)

^c From $S = (X_{m(0)}/X_{n(t)}) - 1$; $X_n = M_n/M_u$.

^d From $\alpha = S/(X_{n(0)} - 1)$.

molecular weight of one (terminal) TDI and $M_u = 2174$, the molecular weight of the unit consisting of 1 (c) plus 1 (d). The extent of degradation α is equal to the fraction of bonds broken, viz.,

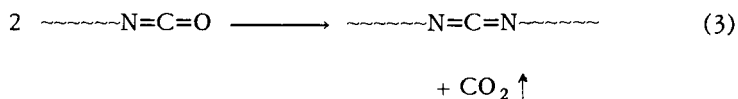
$$\alpha = S/N_b$$

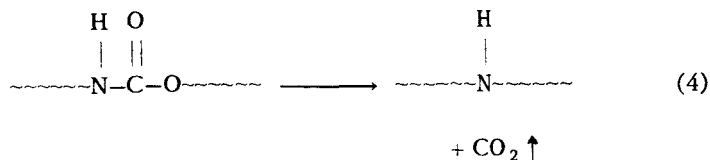
where S is the number of cuts. The probability that a TDI unit will be separated from the chain (excluding chain ends) is the product of the probabilities that two adjacent urethan bonds are cut, α^2 . The probability of obtaining one scission at either end is α . Therefore, the total fraction of urethan bonds that disappear is the product of α^2 and the fraction of adjacent bonds in the molecule excluding chain ends plus the product of α and the fraction of bonds that can be cut at the two ends. Hence:

$$\bar{f} = \alpha^2 \left(\frac{N-2}{N} \right) + 2\alpha/N \quad (2)$$

in which N is the total number of segments of type (c) plus two of type (d), Figure 1. Equation (2) is shown as the solid line in Figure 2. Here N is taken as 15, which corresponds to the number-average molecular weight, M_n , for the polymer with $[\eta] = 0.477$ dl/g. This value of M_n is based on the relationship between $[\eta]$ and M_n established earlier and a knowledge of the molecular weight distribution from fractionation data (1,2). Experimental data are also shown in Figure 2. The method of calculation of the extent of degradation, α , and data for one run are shown in Table I. From Figure 2 the extent of agreement between computed and experimental results may be judged.

Because of the different chemical structures and scission reactions possible, the assumption of equal rates of scission for all bonds containing carbon-14 in PPG-TDI may not be valid. Therefore, deviations of the experimental data from eq. (2) in Figure 2 are to be expected. For example, if one urethan bond attached to the tolyl ring degraded at a much faster rate than the other, α could increase with little or no increase in \bar{f} ; however, this situation is not indicated by the data. In general, for a given number of scissions more carbon-14 is volatilized than is predicted by eq. (1). Carbodiimide or secondary amine formation may occur with loss of labeled CO_2 but without net scissions as follows:





Either of these reactions could result in the observed deviations. Further experiments concerned with the initial scission reactions and quantitative determinations of the volatile products (TDI and CO_2) are in progress.

References

- (1) Rapp, N. S., and J. D. Ingham, J. Polymer Sci., A2, 689 (1964).
- (2) Ingham, J. D., and N. S. Rapp, J. Polymer Sci., in press.
- (3) Ingham, J. D., and N. S. Rapp, J. Org. Chem., in press.

R. Simha

Department of Chemistry
University of Southern California
Los Angeles, California

J. D. Ingham
N. S. Rapp
J. Hardy

Polymer Research Section
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

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